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CANSOC- The Canadian Network for Sampling Organic Compounds in Precipitation

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Abstract

In 1977, the Water Quality Branch, Environment Canada, implemented a sampling network across Canada to determine the concentration of several organochlorine pesticides and PCBs in precipitation. Samples were collected at 12 locations using automatic, wet only collectors. CANSOC data collected between 1977 1980 have shown that wet deposition of airborne trace organic compounds occurs in all regions of Canada. A number of problems with the sampler and the sampling techniques were also identified. Another network, CANSOC II, is being implemented at a number of new sites selected in accordance with new siting criteria. Samples will be recovered at the end of each event and composited monthly, while undergoing extraction with methylene chloride in the field. A set of specifications for an improved sampler and new sampling procedures have been prepared. These specifications will serve as the basis for the design and subsequent construction of a prototype sampler which after testing and evaluation will be phased into the operation of a new national network.

Introduction

CANSOC (Canadian Network for Sampling Organics in Precipitation) was established in 1977 by the Water Quality Branch, Environment Canada to examine precipitation across Canada for the existance and levels of several organochlorine pesticides and PCBs.

In Canada, concern for the atmospheric transport pathway was verified when snow samples from the winter of 1975 76 and rain samples from the period May to November 1976 were collected from the Canadian side of the Great Lakes. All samples were analyzed for polychlorinated biphenyls and a range of organochlorine pesticides. Polychlorinated biphenyls, lindane, α BHC, DDT residues, α endosulfan and β-endosulfan, dieldrin and methoxychlor were

FIGURE 1. CANSOC I AND PROPOSED CANSOC II LOCATIONS

frequently found. The mean rain levels were 21, 5, 12, 3, 7, 1 and 8 ng/L, respectively. Concentrations in snowmelt were generally below the rain values, except for PCBs (Strachan and Huneault, 1979). Murphy and Rzeszutko (1977) determined precipitation inputs of PCBs to Lake Michigan from event precipitation samples collected from November 1975 to October 1976. The average concentration of PCBs in rainfall was 138 ng/L. Further evidence of the atmospheric transport of organic contaminants was shown by Swain (1978), who during the period 1974 through 1976 studied the accumulation of selected persistent organic residues in fish species associated with the nearshore waters of Lake Superior. Swain reported PCB levels of 1.2 mg/kg (wet weight) in lake trout from Lake Siskwit, an interior lake on Isle Royale, Michigan, well removed from the direct influences of man.

Network

The CANSOC network consisted of 12 sampling sites (Figure 1), for the most part located in rural or semi-urban environments. All sites were located at Atmospheric Environment Service (AES), Environment Canada, Surface or Upper Air Weather stations at which complete meteorological data sets are available.

Sample Collectors

Stations in the network were equipped with "modified stainless steel double bucket" Sangamo Type A precipitation collectors. The collector permitted the collection of wet deposition in one bucket and dry deposition in the other. At the onset of a precipitation event an automatic sensing system used to detect precipitation (wet or frozen) initiated the movement of the cover from the "wet" bucket to the "dry" bucket. At the end of the event the cover was automatically returned to the "wet" bucket. On the last day of each month, or if precipitation had occurred that day when the precipitation ceased, the sample was removed from the collector. If the sample was frozen, it was allowed to melt at room temperature prior to being transfered to a pre-cleaned glass bottle.

Samples were then mailed directly to the Inland Waters Directorate, Water Quality Branch Laboratory at the Canada Centre for Inland Waters in Burlington, Ontario for chemical analysis.

Chemical Analysis

The samples were analyzed for organochlorine pesticides and PCBs, Table 1, according to the procedures described in the Water Quality Branch Analytical Methods Manual, 1979. Samples were passed through an XAD-2 resin column and then eluted from the resin column with diethyl ether, followed by concentration using an evaporator. The organic extracts were cleaned and separated into four fractions by means of a high-speed liquid chromotograph. The separated fractions were then quantified by gas liquid chromatographic (GLC) analysis and, in some cases, the analyses were confirmed by mass spectrometric analysis.

Discussion

During the period of operation April 1977-December 1980, sampler malfunctions were responsible for large gaps in the data set for some stations. In many instances, especially for stations in areas having a lower annual precipitation, the sampler did not collect a sufficient sample volume over the collection period to permit an adequate chemical analysis. This necessitated the storage and compositing of the monthly samples for extended periods, which greatly reduced the amount and usefulness of the data available for interpretation. For some of the less water soluble compounds it is highly probable that there was remission to the atmosphere from the sample while it was in the sample container during the collection period (MacKay and Leinonen, 1975). In general, organic compounds in water samples stored in tightly sealed glass containers at 4°C are stable; this cannot be said for the organics in a precipitation sample contained in a loosely sealed collector bucket experiencing a full range of Canadian climatic conditions, over a 30 day sampling period. In addition, precipitation samples generally have a relatively large particulate fraction which presents problems during organic chemical extraction (Coburn 1981).

These factors could explain why the compounds detected most frequently at the highest levels are more water soluble than the compounds detected less frequently. For several of the compounds

Table 1. Table of Compounds Investigated and Criteria for the Protection of Freshwater Aquatic Life

Compound	24 h average value (µg/L)	Maximum value (µg/L)
Heptachlor	0.0038	0.52
Heptachlor epoxide	N.A.	N.A.
α-Chlordane	0.0043*	2.4
γ-Chlordane		
p,p'-Methoxychlor	N.A. (0.03 ug/L)**	N.A
p,p' DDE		
p,p' TDE	0.0010	1.1
p,p' DDT		
o,p'-DDT		
Aldrin	N.A	3.0
Endrin	0.0023	0.18
Dieldrin	0.0019	2.5
Hexachlorobenzene	N.A.	N.A.
Aroclors total	0.014	2.0
α-Endosulfan	0.056	0.22
ß Endosulfan		
γ-BHC	0.080	2.0
α-BHC	N.A.	N.A.
Mirex	N.A. (0.001 ug/L)**	N.A.

* Total concentration of both isomers
** Guidelines for Protection of Freshwater Aquatic Life, USEPA, 1976
N.A. - Not available
Source: USEPA. 1980

Table 2 Percentage of Determinations Greater Than or Equal to the Detection Limit

Compound	Detection limit (ng/L)	Vancouver (20)*	Edson (16)	Fort McMurray (6)	Wynyard (9)	Atikokan (20)	Windsor (21)	Mount Forest (30)	Maniwaki (20)	Chibougamau (16)	Saint-Hubert (11)	Truro (27)	Gander (14)	NAQUADAT parameter code
α-BHC	0.001	75	100	100	100	90	95	88	95	88	92	89	93	14077[illegible]
γ-BHC (lindane)	0.001	75	93	100	100	95	90	78	80	100	83	89	93	18072[illegible]
α-Endosulfan	0.001	45	25	16	11	25	28	36	20	25	45	70	28	18053[illegible]
ß-Endosulfan	0.001	75	43	16	11	15	52	56	60	19	55	63	14	18057[illegible]
p,p'-Methoxychlor	0.001	10	12	0	11	15	86	39	10	6	9	22	7	18033[illegible]
Hexachlorobenzene	0.001	0	6	33	44	15	14	3	5	0	18	4	14	17810[illegible]
Aroclors total (PCBs)	0.02	5	6	16	33	15	28	10	0	12	45	7	31	18276[illegible]
Mirex	0.001	0	0	0	0	0	0	0	0	0	0	0	0	18126[illegible]
p,p'-DDE	0.001	15	6	0	11	10	28	18	10	0	8	15	14	18022[illegible]
p,p'-TDE	0.001	0	0	0	0	0	5	3	10	6	9	4	0	18024[illegible]
p,p'-DDT	0.001	15	6	66	50	40	86	40	16	31	27	24	16	18034[illegible]
o,p'-DDT	0.001	0	0	16	0	5	5	3	5	6	9	7	0	18037[illegible]
Heptachlor	0.001	0	0	0	0	0	0	0	6	0	0	0	0	18047[illegible]
Heptachlor epoxide	0.001	5	6	0	33	15	19	3	5	6	0	15	14	18047[illegible]
Alpha (cis) chlordane	0.001	0	0	0	0	5	14	7	0	0	27	11	7	18062[illegible]
Gamma (trans) chlordane	0.001	5	6	16	44	10	33	6	5	12	0	7	14	18067[illegible]
Aldrin	0.001	-	-	-	-	-	-	3	-	-	-	-	-	18032[illegible]
Endrin	0.001	0	0	0	0	5	5	22	10	12	27	4	7	18142[illegible]
Dieldrin	0.001	10	0	0	55	50	66	55	25	50	45	7	21	18152[illegible]

* Number of samples analyzed is given in parentheses

Table 3 Distribution of Alpha and Gamma-BHC (ng/L)

Station	No. of Samples	α-BHC No. of Values < Detection Limit	α-BHC mean	α-BHC min.	α-BHC max.	γ-BHC (lindane) No. of Values < Detection Limit	γ-BHC (lindane) mean	γ-BHC (lindane) min.	γ-BHC (lindane) max.
Vancouver	20	4	0.0228	<0.001	0.1300	4	0.0052	<0.001	0.0190
Edson	16	0	0.0509	<0.0170	0.0970	1	0.0111	<0.001	0.0220
Fort McMurray	6	0	0.0755	0.0010	0.0500	0	0.0101	0.0030	0.0225
Wynyard	9	0	0.0516	0.0287	0.0870	0	0.0139	0.0077	0.0400
Atikokan	20	1	0.0299	<0.001	0.0680	1	0.0087	<0.001	0.0190
Windsor	21	1	0.0225	<0.001	0.0590	2	0.0075	<0.001	0.0140
Mount Forest	30	4	0.0206	<0.001	0.0690	7	0.0062	<0.001	0.0330
Maniwaki	20	1	0.0264	<0.001	0.0820	4	0.0044	<0.001	0.0107
Chibougamau	16	2	0.0319	<0.001	0.0640	0	0.0066	<0.0020	0.0120
Saint-Hubert	11	1	0.0304	<0.001	0.0720	2	0.0059	<0.001	0.0153
Truro	27	2	0.0172	<0.001	0.0430	3	0.0046	<0.001	0.0140
Gander	14	1	0.0286	<0.001	0.0920	1	0.0045	<0.001	0.0110

under investigation the majority of the results were less than, equal to or slightly above the detection limit. Table 2 summarizes the results in terms of the percentage of analyses greater than or equal to the detection limit. The table shows that α endosulfan, ß endosulfan, α BHC, γ-BHC and p,p'-DDT are frequently found in precipitation samples from all stations, indicating the widespread distribution of these compounds across Canada.

Table 3 shows the distribution of α and γ-BHC. These are the compounds detected most frequently. Generally the mean values for the α -BHC concentrations are much larger than those for γ-BHC. BHC was last registered for use in Canada in 1972. Alpha-BHC has been reported in surface waters, storm waters and precipitation on a wide geographic scale also at levels higher than the γ-BHC form in the environment (Gummer 1979); this may be due to the isomerization of γ BHC to α -BHC in the environment.

As discussed above a number of inadequancies related to the design and operation of the samplers have been identified. Though implemented using 1977 "state of the art" sampling techniques and collectors, the field problems in combination with the problems related to the actual chemical analysis led to the decision to discontinue the original network.

The CANSOC II network presently being developed will function as an interim network operational during the development and evaluation of a new precipitation sampler. The network will be confined to eastern Canada; Ontario, Quebec and the Maritime Provinces (Figure 1). The proposed sampling methodology includes the Sangamo Collector used in the CANSOC network, however, the sampler bucket will be emptied on an event basis into a collection bottle containing methylene chloride. This procedure with allow the extraction process to begin soon after the event rather than in the laboratory a month later. At the end of each calendar month the sample collection bottle will be shipped to the Water Quality Branch - National Laboratory in Burlington, Ontario for analysis. The sampling sites were selected in compliance to siting criteria established as a result of previous study. Sites are located in remote areas, for the most part, to avoid local sources of the organic contaminants under study, ensuring that the data collected are indicative of background levels. Other general siting criteria for precipitation sampling were also meet at each station.

The development of a new sampler for the collection of wet deposition was identified as the most important task in measuring organic compounds in precipitation. Recent research (Strachan and

Huneault, 1982; Eisenreich et al., 1980) has contributed to the development of new methodologies which collectively provided background information for the design of a better sampler.

Specifically, the sampler must be able to operate automatically in remote locations in the severity of the Canadian climate. In addition, sampler collection efficiency must be maximized for both wet and frozen precipitation. This seems to be a difficult problem to solve because in general the aerodynamics of snowfall collection are different from those for rain collection. To optimize collection efficency for wet and frozen precipitation, it may be necessary to design and construct two different samplers.

Automatic sample extraction at the site during the precipitation event has been recognized as a top priority for consideration in the design of the new sampler. Two methods, resin extraction and solvent extraction, have been considered.

Solvent extraction using methylene chloride is considered to be very efficient; it does provide good recoveries for a wide range of organic compounds. Unfortunately it is difficult to use in the field, especially for non-professional staff as it contaminantes easily. In addition, solvent extraction requires a sample storage extraction container which must endure the rigors of the field and shipping to the laboratory.

Resin extraction, using Teflon columns, are easier to use in both the field and during laboratory procedures. Shipping problems are alleviated and the possibility of contamination is greatly reduced. Resins have been used in the field (Strachan, Huneault, 1982) and recoveries for a number of organic compounds have been found to be acceptable. Certain resins are better suited for the extraction of some classes of compounds than others. This implies that different resin columns or a mixed resin bed may be necessary for extracting a wide range of organic compounds from precipitation.

The new sampler specifications call for a resin column extraction system with a configuration which allows up to three extracting columns in series or parallel. This will allow columns packed with different resins, thus expanding the range of compounds that the sampler can efficiently be used to sample. The optional column configuration can also be used for quality control, e.g. taking replicate samples. The new sampler will also record the total amount of water which passes through the columns for each event together with the beginning and the end (hour, minute, day, month) of each event.

A contract for building a prototype sampler according to these specifications is now in progress. The prototype sampler will be evaluated in the laboratory and in the field. The laboratory evaluation includes testing for component durability, finding the appropriate resins and studying the reproducibility of organic compound recovery data. Once the prototype sampler has successfully meet the design criteria other samplers will be produced and gradually introduced into the national network.

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